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1. I am a citizen of Japan residing at 24-5, Mejirodai 4-chome, Hachioji-shi, Tokyo, Japan.

2. To the best of my ability, I translated

**Japanese Patent Application No. 10-73998**

from Japanese into English and the attached document is a true and accurate English translation thereof.

3. I further declare that all statements made herein are true, and that all statements made on information and belief are believed to be true; and further that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Date: June 24, 2002

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【書類名】 特許願 特願平10-73998  
【整理番号】 JK97122  
【提出日】 平成10年03月23日  
【あて先】 特許庁長官殿  
【国際特許分類】 C04B 35/26  
【発明の名称】 フェライト磁石の製造方法  
【請求項の数】 3  
【発明者】

2/5

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【手数料の表示】

【予納台帳番号】 010375

【納付金額】 21000

【提出物件の目録】

【物件名】 明細書 1

【物件名】 要約書 1

**Japanese Patent Application No. 10-73998**

**Document**            Application for Patent  
**Ref. No.**            JK97122  
**Filing Date**        March 23, 1998  
**To:**                  Commissioner of The Patent Office  
**IPC**                  C04B 35/26

**Title of the Invention**

METHOD FOR PRODUCING FERRITE MAGNET

**Number of Claims**            3

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21,000

**Attached Papers**

Specification                    one  
ABSTRACT                        one

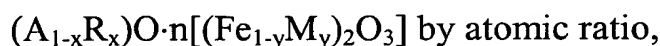
## SPECIFICATION

### Title of the Invention

#### METHOD FOR PRODUCING FERRITE MAGNET

#### 5 Claims

1. A method for producing a ferrite magnet having a basic composition represented by the following general formula:



wherein A is at least one of Sr and Ba, R is at least one element selected  
10 from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least one element selected from the group consisting of Mn, Co, Ni and Zn, and x, y and n are numbers meeting the following conditions:

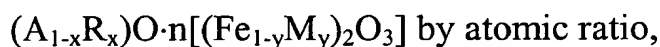
$$0.05 \leq x \leq 0.5,$$

15  $[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$

$$5.4 \leq n \leq 6.0,$$

said method using a hydroxide, a carbonate or a salt of organic acid of La as a raw material for supplying La.

2. A method for producing a ferrite magnet having a basic  
20 composition represented by the following general formula:



wherein A is at least one of Sr and Ba, R is at least one element selected from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least one element selected from the group consisting of  
25 Mn, Co, Ni and Zn, and x, y and n are numbers meeting the following

conditions:

$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5.4 \leq n \leq 6.0,$$

5    said method using a hydroxide or a carbonate of Co as a raw material for supplying Co.

3.    The method for producing a ferrite magnet according to claim 1 or 2, said method comprising mixing, calcinating, coarsely pulverizing, finely pulverizing, molding, sintering, and working, wherein said raw material for  
10    supplying La and/or Co is added at the time of finely pulverizing.

## DETAILED DESCRIPTION OF THE INVENTION

[0001]

### Field of the Invention

The present invention relates to a method for producing a  
5 high-performance ferrite magnet useful for wide ranges of magnet  
applications and having a higher saturation magnetization ( $\sigma_s$ ) and higher  
coercivity (iHc) than those of the conventional ferrite magnets.

[0002]

### Prior Art

10 Ferrite magnets are widely used in various applications including  
rotors of motors, electric generators, etc. Recently, ferrite magnets having  
higher magnetic properties are required particularly for the purposes of  
miniaturization and reduction in weight in the field of rotors for  
automobiles and increase in performance in the field of rotors for electric  
15 apparatuses.

High-performance sintered magnets such as Sr ferrite or Ba ferrite  
are conventionally produced through the following processes. First, iron  
oxide is mixed with a carbonate, etc. of Sr or Ba and then calcined to cause  
a ferritization reaction (ferrite-forming reaction). The resultant calcined  
20 clinker is coarsely pulverized, mixed with  $\text{SiO}_2$ ,  $\text{SrCO}_3$ , and  $\text{CaCO}_3$  for  
controlling sintering behavior and  $\text{Al}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ , etc. for controlling iHc,  
and then finely pulverized to an average diameter of 0.7-1.0  $\mu\text{m}$ . A slurry  
containing the finely pulverized ferrite-forming material is wet-molded  
while being oriented in a magnetic field to obtain a mold. The resultant  
25 mold is sintered and then machined to a desired shape.

To increase the properties of the ferrite magnets produced according to the method mentioned above as a prerequisite, there are the following five methods available.

The first method is a fine pulverization method. When the size of  
 5 crystal grains in the sintered body is close to about  $0.9\ \mu\text{m}$ , a critical single magnetic domain diameter of a magnetoplumbite (M)-type Sr ferrite magnet, its  $iH_c$  is maximum. Accordingly, fine pulverization may be carried out to an average diameter of  $0.7\ \mu\text{m}$  or less, for instance, taking into consideration the crystal grain growth at the time of sintering. This  
 10 method is, however, disadvantageous in that finer pulverization leads to poorer water removal at the time of wet molding, resulting in poorer production efficiency.

The second method is to make the sizes of the crystal grains in the sintered body as uniform as possible. Ideally, the sizes of the crystal  
 15 grains are made as uniformly as possible equal to the above critical single magnetic domain diameter (about  $0.9\ \mu\text{m}$ ), because crystal grains larger than or smaller than this size have low  $iH_c$ . Specific means for achieving high performance in this method is to improve a particle size distribution of fine powder. In commercial production as a prerequisite, however, other  
 20 pulverization apparatuses than ball mills, attritors, etc. cannot but be used, naturally posing limitations in the level of improvement. Also, an attempt was recently published to produce fine ferrite powder having a uniform particle size by a chemical precipitation method. Such method is, however, not suitable for industrial mass production.

25 The third method is to improve crystal orientation affecting

magnetic anisotropy. Specific means in this method is to improve the dispersion of ferrite particles in a slurry of fine powder by adding a surfactant, or to increase the intensity of a magnetic field at the time of orientation, etc.

5           The fourth method is to improve the density of a sintered body. A Sr ferrite sintered body has a theoretical density of 5.15 g/cc. Sr ferrite magnets commercially available at present have densities ranging from 4.9 g/cc to 5.0 g/cc, corresponding to 95-97% of the theoretical density. Although improvement in Br is expected by increasing the density of a  
10 ferrite magnet, a higher density than the above level needs such density-increasing means as HIP, etc. However, the use of such density-increasing means leads to increase in the production cost of ferrite magnets, depriving the ferrite magnets of advantages as inexpensive magnets.

15           The fifth method is to improve a saturation magnetization  $\sigma_s$  or a crystal magnetic anisotropy constant of a ferrite compound per se, which is a main component of the ferrite magnet. It is likely that the improvement in the saturation magnetization  $\sigma_s$  directly leads to improvement in the residual magnetic flux density Br of the ferrite magnet. It is also likely  
20 that the improvement in the crystal magnetic anisotropy constant leads to improvement in the coercivity Hc of the ferrite magnet.

As a result of intense research to achieve the increase in the properties of the ferrite magnet mentioned above, the inventor has found a new ferrite magnet excellent remarkably in magnetic properties and a  
25 fundamental method for producing thereof based on the above fifth method.



Namely, there has been found a method to replace part of A and Fe elements in the above ferrite composition with other elements by adding other types of metal compounds to a ferrite composition expressed by  $AO \cdot nFe_2O_3$ , wherein A is at least one of Sr and Ba, whereby the above compounds of La and/or Co are particularly effective.

[0003]

### Problems to be Solved by the Invention

In the course to conduct further investigation using oxides of La and Co, that is,  $La_2O_3$  and  $Co_3O_4$ , the inventor has found that the solid phase reaction of  $La_2O_3$  or  $Co_3O_4$  with a mixture of  $Co_3O_4$  and  $SrCO_3 + Fe_2O_3$ , or the solid phase reaction of La with a ferrite composition does not proceed completely. In other words, the diffusion rate of La or Co element in the ferrite composition is slow to cause a microstructure having a non-uniform distribution of La or Co in the obtained sintered body, whereby the effectiveness of replacement with La and Co has not been sufficiently provided. When the content of La and Co is different in the respective crystal grains in the sintered body, there is caused a distribution in coercivity ( $iH_c$ ), resulting in a poor squareness of the hysteresis curve to decrease the maximum energy product, which is a barometer of the magnetic energy obtained from a magnet.

Therefore, the object of the present invention is to make the distribution of La and Co in the structure uniform and provide a method for producing ferrite magnets with improved magnetic properties.

[0004]

### Means to Solve the Problems

To achieve the above object, the inventor has found a method carrying the purpose to use more reactive compounds to provide finer primary crystal grains than conventional oxides ( $\text{La}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ) as the La and/or Co addition compounds.

5 In producing oxides ceramics by using a powder metallurgical method, the reactivity may be improved when the addition compound is not an oxide but a hydroxide, carbonate or salt of organic acid.

The first reason is that the hydroxide, carbonate or salt of organic acid can easily provide a powder having finer grain size as compared with  
10 the oxide. The second reason is that the first crystal grains are finely pulverized to improve the reactivity when it is decomposed and converted to the oxide in the process of elevating temperature at the time of calcinating or sintering step. The third reason is that the above decomposition reaction per se may also improve the reactivity.

15 With the above in mind, an enormous research has been conducted in detail for the purpose of improving the reactivity by adding various La or Co compounds. As a result, it has been found that a hydroxide, a carbonate, or a salt of organic carboxylic acid of La and/or Co in place of an oxide thereof is sufficiently usable, particularly, the hydroxide is  
20 effective. The present invention is accomplished based on this finding.

[0005]

Thus, the present invention is method for producing a ferrite magnet having a basic composition represented by the following general formula:

$(\text{A}_{1-x}\text{R}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3]$  by atomic ratio,

25 wherein A is at least one of Sr and Ba, R is at least one element selected

from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least one element selected from the group consisting of Mn, Co, Ni and Zn, and x, y and n are numbers meeting the following conditions:

$$\begin{aligned} 5 \quad & 0.05 \leq x \leq 0.5, \\ & [x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and} \\ & 5.4 \leq n \leq 6.0, \end{aligned}$$

the method using a hydroxide, a carbonate or a salt of organic acid of La as a material for supplying La, and also the method using a hydroxide, a  
10 carbonate or a salt of organic acid of Co as a material for supplying Co.

Preferable as materials for supplying La are  $\text{La}(\text{OH})_3$  (hydroxide),  $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$  (hydrate of carbonate),  $\text{La}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5\text{H}_2\text{O}$  or  $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  (organic acid salt), particularly,  $\text{La}(\text{OH})_3$  (hydroxide) providing a preferable result.

15 Preferable as materials for supplying Co are  $\text{Co}(\text{OH})_2$  or  $\text{Co}_3\text{O}_4 \cdot x\text{H}_2\text{O}$  (hydroxide),  $\text{CoCO}_3$  (carbonate). Besides them, it is possible to use  $x\text{CoCO}_3 \cdot y\text{Co}(\text{OH})_2 \cdot z\text{H}_2\text{O}$  (basic cobalt carbonate).

Also, with respect to other elements relating to the present invention, that is, Nd, Pr and Zn, Mn, Ni, when their hydroxides,  
20 carbonates, or salts of organic acid are used in place of their oxides, there may be provided preferable results.

[0006]

The above compounds for supplying replacing elements can be added at mixing step in the following standard process for producing ferrite  
25 magnets:

Mixing → calcination → pulverization → molding → sintering → working.

That is, the compounds of La and Co elements are to undergo two time heating at a high temperature at the time of calcination and sintering by adding at the time of mixing in the above steps, whereby the solid diffusion proceeds to provide a uniform composition. However, it is sometimes not suitable for industrial mass production to add at the time of mixing from the viewpoint of dividing lots, etc. In this case, it is not substantially destroy the effects of the present invention to obtain the ferrite magnet composition according to the present invention by adding the above compounds of La and/or Co at the time of pulverizing in the above standard process for producing. The sufficient effects of using the La or Co compounds relating to the present invention can be relatively appreciated in the case of addition at the time of pulverizing. This is because a ferrite composition undergoes only one high-temperature process, particularly a sintering process, whereby high reactivity of hydroxides, carbonates or organic acid salts is much more effective than in the case of conventional oxides.

Also, in the case of adding the above hydroxide of La and/or Co, it is likely that the addition of the hydroxide powder thereof may be replaced, for instance, with the addition of hydroxide of La and/or Co formed by adding an alkaline material such as NaOH, NH<sub>4</sub>OH, etc. to a dispersion of ferrite material powder in a CoCl<sub>2</sub> aqueous solution prepared in advance, whereby the effects of the present invention are not disturbed.

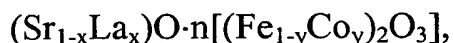
[0007]

## Operative Embodiments for Practicing the Invention

The present invention will be described in detail below referring to EXAMPLES.

### [EXAMPLE 1]

5             $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}(\text{OH})_3$  (hydroxide) and  $\text{Co}_3\text{O}_4$  (oxide) were formulated to provide a basic composition represented by the following formula:



wherein  $n = 5.9$ ,  $x = 2ny$ , and  $x = 0.15$ , wet-mixed, and then calcined at  
 10     $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of  $0.7\text{-}0.8\ \mu\text{m}$  in average diameter. On this occasion, added at an early stage of the pulverization of each coarse powder were 0.50 weight % of  $\text{SrCO}_3$ , 0.80  
 15    weight % of  $\text{CaCO}_3$  and 0.45 weight % of  $\text{SiO}_2$ , based on the weight of the coarse powder. The resultant fine powder slurry was wet-molded in a magnetic field of 10 kOe, and each of the resultant green bodies was sintered at  $1180\text{-}1230^\circ\text{C}$  for 2 hours. Each of the resultant sintered bodies was machined to a shape of about  $10\text{ mm} \times 10\text{ mm} \times 20\text{ mm}$  to measure  
 20    magnetic properties by a B-H tracer.

As COMPARATIVE EXAMPLE, a ferrite composition in which  $n = 6.0$  and  $x = 0$  (La and Co: not added), and  $x = 0.15$  in the above basic composition using  $\text{La}_2\text{O}_3$  (oxide) and  $\text{Co}_3\text{O}_4$  (oxide) was calcined in the same manner. The results are shown in Table 1. Incidentally, in Table 1,  
 25    Br is residual magnetic flux density,  $iH_c$  is coercivity, and  $H_k$  is a value of

H when the M value becomes 95% of the Mr (Br) value at a position in the second quadrant of a M (magnetization) – H (intensity of magnetic field) hysteresis curve. A value of Hk/iHc represents the squareness ratio of the above hysteresis curve, and it seems that the value per se represents not  
5 only practically a important magnetic property but also is a barometer showing the uniformity of the distribution of La and Co elements in the sintered body.

It is appreciated from the comparison between Comparative Example B and Example A in Table 1 that when La(OH)<sub>3</sub> was used in place  
10 of conventional La<sub>2</sub>O<sub>3</sub> as a method of adding the La element, Br and iHc were improved, particularly, the Hk/iHc value showing a squareness ratio was remarkably improved. As shown in this EXAMPLE, it is clear that the method according to the present invention is advantageous over the conventional methods.

15

[0008]

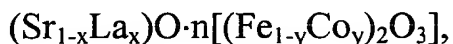
Table 1

No.	x	La	Co	Sintering Temp. (°C)	Br (G)	iHc (Oe)	Hk/iHc (%)
Com.	0.00	-	-	1200	4115	3505	95.7
Ex.				1210	4155	3395	96.1
A				1220	4185	3330	97.3
Com.	0.15	La <sub>2</sub> O <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	1210	4210	4395	90.6
Ex.				1220	4245	4350	91.0
B				1230	4270	4155	92.3
Ex.	0.15	La(OH) <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	1210	4225	4430	94.2
A				1220	4265	4380	94.8
				1230	4285	4185	95.3
Ex.	0.15	La <sub>2</sub> O <sub>3</sub>	Co(OH) <sub>2</sub>	1210	4215	4435	93.9
B				1220	4260	4385	94.8
				1230	4280	4210	95.0

[0009]

## [EXAMPLE 2]

SrCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> (oxide) and Co(OH)<sub>2</sub> (hydroxide) were formulated to provide a basic composition represented by the following formula:



wherein  $n = 5.9$ ,  $x = 2ny$ , and  $x = 0.15$ , wet-mixed, and then calcined at 1200°C for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of 0.8 μm in average diameter. On this occasion, added at an early stage of the pulverization of each coarse powder were 0.50 weight % of SrCO<sub>3</sub>, 0.80 weight % of CaCO<sub>3</sub> and 0.45 weight % of SiO<sub>2</sub>, based on the weight of the coarse powder. The resultant fine powder slurry was wet-molded in a magnetic field of 10 kOe, and each of the resultant green bodies was sintered at 1180-1230°C for 2 hours. Each of the resultant sintered bodies was machined to a shape of about 10 mm × 10 mm × 20 mm to measure magnetic properties by a B-H tracer. The results are shown in Table 1.

It is appreciated from the comparison between Comparative Example B and Example B in Table 1 that when Co(OH)<sub>2</sub> was used in place of conventional Co<sub>3</sub>O<sub>4</sub> as a method of adding the Co element, Br and iHc were improved, particularly, the Hk/iHc value showing a squareness ratio was remarkably improved. As shown in this EXAMPLE, it is clear that the method according to the present invention is advantageous over the conventional methods.



[0010]

[EXAMPLE 3]

SrCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were formulated to provide a basic composition of SrO·nFe<sub>2</sub>O<sub>3</sub>, wherein n = 5.9, wet-mixed, and then calcined at 1200°C  
5 for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of 0.7-0.8 μm in average diameter. On this occasion, La(OH)<sub>3</sub> (hydroxide) and Co(OH)<sub>2</sub> (hydroxide) were added at an early stage of the fine pulverization of each  
10 coarse powder. Further, 0.50 weight % of SrCO<sub>3</sub>, 0.80 weight % of CaCO<sub>3</sub> and 0.45 weight % of SiO<sub>2</sub>, based on the weight of the coarse powder, were added as sintering aids at an early stage of the fine pulverization of each coarse powder. Each of the resultant two fine powder slurries was wet-molded in a magnetic field of 10 kOe, and each of  
15 the resultant green bodies was sintered at 1180-1230°C for 2 hours. Each of the resultant sintered bodies was machined to a shape of about 10 mm × 10 mm × 20 mm to measure magnetic properties by a B-H tracer.

As COMPARATIVE EXAMPLE, a ferrite composition using La<sub>2</sub>O<sub>3</sub> (oxide) and Co<sub>3</sub>O<sub>4</sub> (oxide) was calcined in the same manner, thereafter  
20 followed by steps in the same manner as mentioned above to evaluate the magnetic properties. The results are shown in Table 2.

It is appreciated from the comparison between Comparative Example C and Example C in Table 2 that when La(OH)<sub>3</sub> and Co(OH)<sub>2</sub> were used, respectively, in place of conventional oxides as a method of  
25 adding a La element and a Co element, magnetic properties were improved,

particularly, the iHc value was remarkably improved. As shown in this EXAMPLE, it is clear that the method according to the present invention is advantageous over the conventional methods.

[0011]

5

Table 2

No.	x	La	Co	Sintering Temp. (°C)	Br (G)	iHc (Oe)	Hk/iHc (%)
Com.	0.00	-	-	1200	4115	3505	95.7
Ex.				1210	4155	3395	96.1
A				1220	4185	3330	97.3
Com.	Cor.*)	La <sub>2</sub> O <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	1210	4125	3875	94.7
Ex.	to			1220	4160	3815	95.1
C	0.15			1230	4190	3765	95.6
Ex.	Cor.*)	La(OH) <sub>3</sub>	Co(OH) <sub>2</sub>	1210	4120	4285	94.8
C	to			1220	4165	4225	95.3
	0.15			1230	4200	4180	96.1

\*) Cor. to = Corresponding to

[0012]

The EPMA analysis were performed with respect to several points of a cross-sectional structure of each magnet of the above EXAMPLES and COMPARATIVE EXAMPLE under the same conditions, respectively. As a result, it is appreciated that the distribution of La and Co of the EXAMPLE is remarkably uniform as compared with that of the COMPARATIVE EXAMPLE.

[0013]

**Effects of the Invention**

As mentioned above, according to the present invention, it is possible to produce a ferrite magnet significantly excellent in magnetic properties as compared with those of conventional ferrite magnets, thereby  
5 greatly contributing to the development in the wide ranges of magnet applications as a new ferrite magnet excellent in cost performance.

## ABSTRACT

### Problems to be solved:

To provide a method for producing a ferrite magnet having the  
5 distribution of a La element and a Co element in the structure uniform with  
excellent magnetic properties

### Solution:

A method for producing a ferrite magnet having a basic  
composition represented by the following general formula:

10  $(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,  
wherein A is at least one of Sr and Ba, R is at least one element selected  
from the group consisting of La, Nd and Pr, La being an indispensable  
element, M is at least one element selected from the group consisting of  
Mn, Co, Ni and Zn, and x, y and n are numbers meeting the following  
15 conditions:

$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5.4 \leq n \leq 6.0,$$

the method using a hydroxide, a carbonate, or a salt of organic acid of La as  
20 a raw material for supplying La.

**Selected Drawings:** Non.

## SPECIFICATION

## Title of the Invention

## FERRITE MAGNET AND METHOD FOR PRODUCING SAME

## 5 Claims

1. A ferrite magnet having a basic composition represented by the following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one element selected from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least one element selected from the group consisting of Mn, Co and Ni, and x, y and n are numbers meeting the following conditions:

$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5.4 \leq n \leq 6.0.$$

2. The ferrite magnet according to claim 1, further comprising 0.20-0.50 weight % of SiO<sub>2</sub> and 0.35-0.55 weight % of CaO per said basic composition.

20 3. A ferrite magnet having a basic composition represented by the following general formula:

$(A_{1-x}R_x)O \cdot n[(Fe_{1-y}M_y)_2O_3]$  by atomic ratio,

wherein A is at least one of Sr and Ba, R is at least one element selected from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least two elements selected from the group consisting of

Mn, Co, Ni and Zn, Co being an indispensable element, and x, y and n are numbers meeting the following conditions:

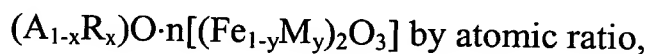
$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

5  $5.4 \leq n \leq 6.0.$

4. The ferrite magnet according to claim 2, further comprising 0.20-0.50 weight % of SiO<sub>2</sub> and 0.35-0.55 weight % of CaO per said basic composition.

5. A method for producing a ferrite magnet having a basic  
10 composition represented by the following general formula:



wherein A is at least one of Sr and Ba, R is at least one element selected from the group consisting of La, Nd and Pr, La being an indispensable element, M is at least one element selected from the group consisting of  
15 Mn, Co and Ni, and x, y and n are numbers meeting the following conditions:

$$0.05 \leq x \leq 0.5,$$

$$[x/(2.4n)] \leq y \leq [x/(1.6n)], \text{ and}$$

$$5.4 \leq n \leq 6.0,$$

20 said method comprising the steps of subjecting a raw material powder having said basic composition to pulverizing to a fine powder having an average diameter ranging 0.4-0.7  $\mu$ m, drying or concentrating, milling, molding in a magnetic field and sintering.

6. The method producing a ferrite magnet according to claim 5,  
25 wherein 0.2-2.0 weight % of a dispersant per a solid component is added at

[EXAMPLE 3]

To investigate the permissible range of a ratio of the R element to the M element added in connection with charge compensation, Sr, La and Co were selected as the A element, the R element and the M element, respectively, and SrCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and CoO were formulated in such proportions as to provide the following basic composition:

(Sr<sub>1-x</sub>La<sub>x</sub>)O·n[(Fe<sub>1-y</sub>Co<sub>y</sub>)<sub>2</sub>O<sub>3</sub>] by atomic ratio,  
wherein  $n = 6.0$ ,  $y = 0.77-1.43 \times 10^{-2}$ , and  $x = 0.15$ ,

wet-mixed, and then calcined at 1200°C for 2 hours. Thereafter, the coarse powder was produced by the method in the same manner as in EXAMPLE 1, and the magnetic properties of the resultant coarse powder were measured.

It has thus been found that there is no substantial deterioration in magnetic properties, as long as the ratio of  $x/ny$  is within the range of 1.6-2.4, not limited to the conditions under which the charge balance is fully kept, namely to a ratio of  $x$  to  $y$  satisfying the relation of  $y = x/2n$ . On the other hand, when the ratio of  $x/ny$  exceeds 2.4 or is less than 1.6, remarkable decrease in magnetic properties is appreciated. Accordingly, the ratio of  $x/ny$  should be preferably between 1.6 and 2.4. This condition may be converted to the formula of  $y$  as a preferable range of the value of  $y$  as follows:

$$[x/(2.4n)] \leq y \leq [x/(1.6n)].$$

[0012]

[EXAMPLE 4]

Sr, La and Co were selected as the A element, the R element and the

M element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{ZnO}$  were formulated to provide the following basic composition:

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n[(\text{Fe}_{1-y}\text{Zn}_y)_2\text{O}_3]$  by atomic ratio,

wherein  $n = 5.85$ ,  $x = 2ny$  and  $x = 0.117$ ,

5 wet-mixed, and then calcined at  $1200^\circ\text{C}$  for 2 hours in the air. The calcined powder was coarsely pulverized in a dry state by a roller mill, and then finely pulverized in a wet state by an attritor to produce a slurry containing fine powder of  $0.7\ \mu\text{m}$  in average diameter. Added as sintering aids at an early stage of the fine pulverization of the coarse powder were  
10 0-0.60 weight % of  $\text{SiO}_2$  and 0.80 weight % of  $\text{CaCO}_3$  (0.45 weight % as  $\text{CaO}$ ), based on the weight of the coarse powder. Each of the resultant fine powder slurries was wet-molded in a magnetic field of 10 kOe, and each of the resultant green bodies was sintered at  $1180\text{-}1230^\circ\text{C}$  for 2 hours. Each of the resultant sintered bodies was machined to a shape of about 10  
15  $\text{mm} \times 10\ \text{mm} \times 20\ \text{mm}$  to measure magnetic properties by a B-H tracer. The results are shown in Fig. 2. Incidentally, when  $\text{SiO}_2$  was 0 weight %, the value of  $i\text{Hc}$  was extremely too low to plot it.

It is clear from Fig. 2 that as the amount of  $\text{SiO}_2$  added increases, the  $i\text{Hc}$  increases, and when the amount of  $\text{SiO}_2$  added is 0.45 weight %, an  
20 appropriate value of  $i\text{Hc}$  is obtained. On the other hand, when the amount of  $\text{SiO}_2$  added increases to 0.60 weight %, the dependency of  $i\text{Hc}$  on the sintering temperature becomes unstable. This seems because the effect of  $\text{SiO}_2$  to suppress the crystal grain growth is excessively suppressed so that proper grain growth does not take place at the sintering step. Accordingly,  
25 it is understandable that the amount of  $\text{SiO}_2$  added is preferably between



0.40 and 0.50 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %.

The above results were obtained in the case of  $n = 5.85$ . However, since the range of the amount of  $\text{SiO}_2$  added depends on the value of  $n$ ,

5 similar investigations have been carried out when the value of  $n$  is 5.95.

In this case ( $n = 5.95$ ), it has been found that the amount of  $\text{SiO}_2$  added is preferably between 0.20 and 0.50 weight %.

The dependency of magnetic properties on the amount of  $\text{CaO}$  added has been investigated, when the amount of  $\text{SiO}_2$  added is fixed to be  
10 0.45 weight %. The results are substantially same as those mentioned above. As a result, it has been found that the amount of  $\text{CaO}$  added is preferably between 0.35 and 0.55 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %.

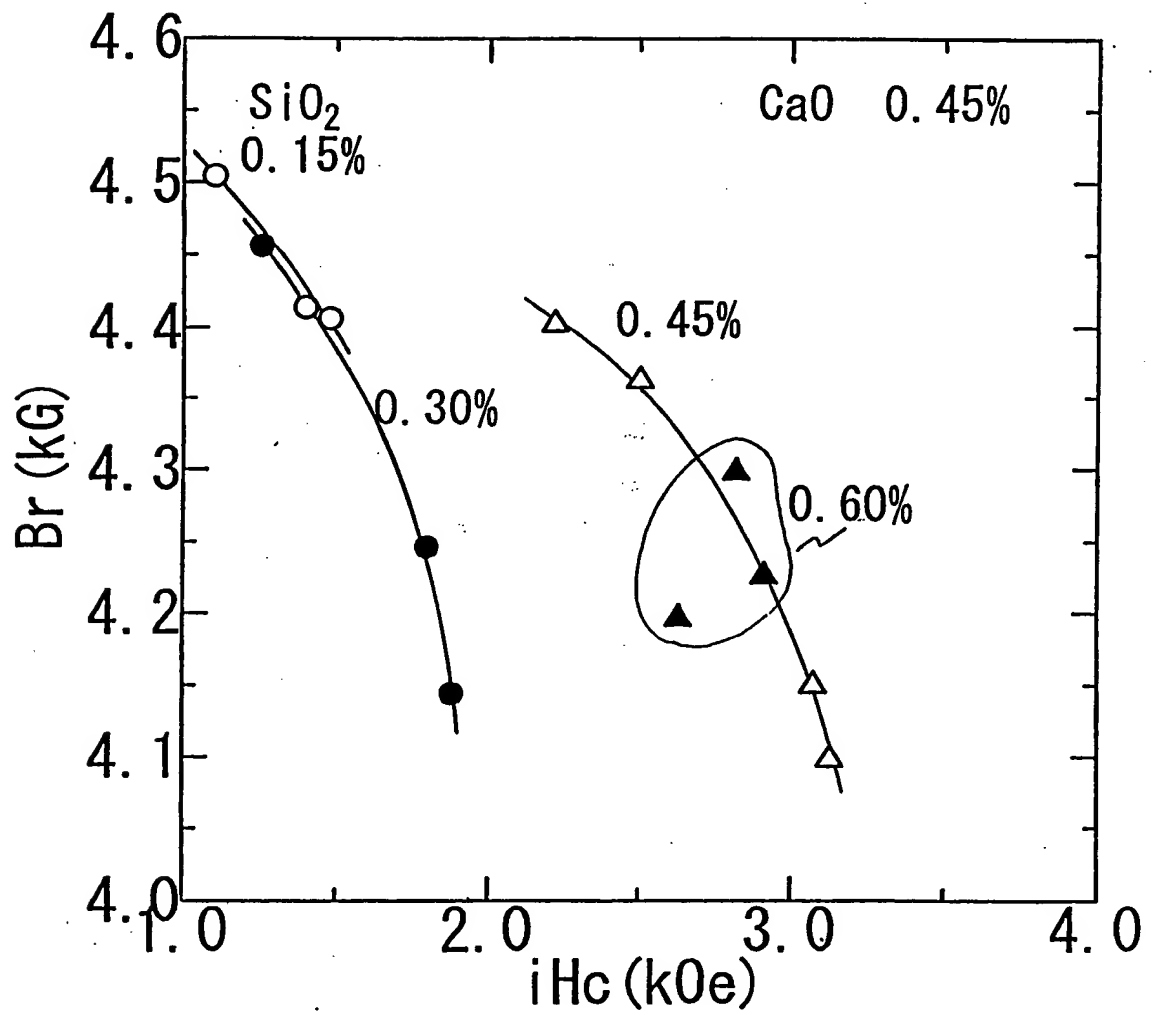
Next, as the results of investigation in connection with the influence  
15 of the amount of the combined addition of  $\text{SiO}_2$  and  $\text{CaO}$  on the magnetic properties of the sintered body produced by the method in the same manner as in EXAMPLE 4 except that  $\text{Co}$  was selected in place of  $\text{Zn}$  as the  $\text{M}$  element, it has been found that the amount of  $\text{SiO}_2$  added is between 0.20 and 0.50 weight % and the amount of  $\text{CaO}$  added is between 0.35 and 0.50  
20 weight %, assuming that the basic composition of the ferrite magnet is 100 weight %.

[0013]

[EXAMPLE 5]

La was selected as the  $\text{R}$  element, and  $\text{Mn}$ ,  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Zn}$  were  
25 selected as the  $\text{M}$  element, respectively, and  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and

FIG. 2



【書類名】 明細書

【発明の名称】 フェライト磁石およびその製造方法

【特許請求の範囲】

【請求項 1】 原子比率で  $(A_{1-x}R_x)O \cdot n ((Fe_{1-y}M_y)_2O_3)$

(ここで A は S r、B a のうち少なくとも 1 種以上、R は L a、N d、P r のうち少なくとも 1 種以上であって L a を必ず含む、M は M n、C o、N i のうち少なくとも 1 種以上)、

$$0.05 \leq x \leq 0.5$$

$$(x / (2.4 n)) \leq y \leq (x / (1.6 n))$$

$$5.4 \leq n \leq 6.0$$

なる基本組成を有することを特徴とするフェライト磁石。

【請求項 2】 前記基本組成物に対して重量百分比率で 0.20 ~ 0.50 % の  $SiO_2$  および 0.35 ~ 0.55 % の  $CaO$  を含有する請求項 1 に記載のフェライト磁石。

【請求項 3】 原子比率で  $(A_{1-x}R_x)O \cdot n ((Fe_{1-y}M_y)_2O_3)$

(ここで A は S r、B a のうち少なくとも 1 種以上、R は L a、N d、P r のうち少なくとも 1 種以上であって L a を必ず含む、M は M n、C o、N i、Z n のうち少なくとも 2 種以上であって C o を必ず含む)、

$$0.05 \leq x \leq 0.5$$

$$(x / (2.4 n)) \leq y \leq (x / (1.6 n))$$

$$5.4 \leq n \leq 6.0$$

なる基本組成を有することを特徴とするフェライト磁石。

【請求項 4】 前記基本組成物に対して重量百分比率で 0.20 ~ 0.50 % の  $SiO_2$  および 0.35 ~ 0.55 % の  $CaO$  を含有する請求項 3 に記載のフェライト磁石。

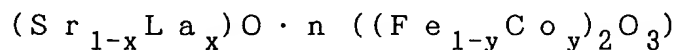
【請求項 5】 原子比率で  $(A_{1-x}R_x)O \cdot n ((Fe_{1-y}M_y)_2O_3)$

(ここで A は S r、B a のうち少なくとも 1 種以上、R は L a、N d、P r のうち少なくとも 1 種以上であって L a を必ず含む、M は M n、C o、N i のうち少なくとも 1 種以上)、 $0.05 \leq x \leq 0.5$ 、 $(x / (2.4 n)) \leq y \leq (x / (1.$

【0010】

## (実施例2)

A元素としてSr、R元素としてLa、M元素としてCoをそれぞれ選択し、 $\text{SrCO}_3$ 、 $\text{Fe}_2\text{O}_3$ 、 $\text{La}_2\text{O}_3$ およびCoOを下記に示す化学式において、 $n = 6.0$ 、 $x = 2ny$ 、 $x = 0 \sim 0.6$ になるよう配合し、湿式にて混合した後、 $1200^\circ\text{C}$ で



2時間、大気中で仮焼した。その後実施例1に示したのと同様な方法により粗粉碎粉を作製し、磁気特性を評価した。その結果を図1に示す。図1より $\text{La}_2\text{O}_3$ およびCoOを同時に加えることにより、保磁力が顕著に向上することが明確にわかる。また飽和磁化はほぼその値を維持あるいは顕著な減少を示さないことがわかる。また添加量x値が0.05以上でその効果が顕著となり、0.5を越えると効果が減じることがわかる。従ってx値に関しては、0.05以上、0.5以下が望ましく、更に望ましくは0.07以上、0.4以下である。

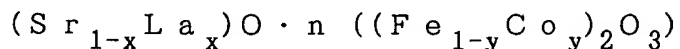
R元素がLa+Pr、La+NdおよびM元素がCo+Zn、Co+Mn、Co+Niの場合においても図1とほぼ同様な傾向が認められた。

またn値が5.4～6.0の範囲では有意に差異は認められず、同様な効果が得られることを確認した。

【0011】

## (実施例3)

電荷補償と関連して、R元素とM元素の添加量比の許容範囲を求める検討を行った。A元素としてSr、R元素としてLa、M元素としてCoをそれぞれ選択し、 $\text{SrCO}_3$ 、 $\text{Fe}_2\text{O}_3$ 、 $\text{La}_2\text{O}_3$ およびCoOを下記に示す化学式において、 $n = 6.0$ 、 $y = 0.77 \sim 1.43 \times 10^{-2}$ 、 $x = 0.15$ になるよう配合し、湿式にて



混合した後、 $1200^\circ\text{C}$ で2時間、大気中で仮焼した。その後実施例1に示したのと同様な方法により粗粉碎粉を作製し、その磁気特性を評価した。

その結果、電荷バランスが完全に満たされた条件、即ち $x = 2ny$ が成り立つ

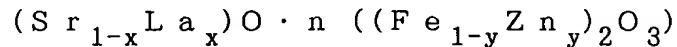
添加量比のみならず、 $x / n y$  値が 1.6 から 2.4 の範囲にあれば、磁気特性の実質的な劣化は認められず、本発明の効果が維持されることがわかる。一方、 $x / n y$  値が 2.4 を越えた場合あるいは 1.6 未満の場合には磁気特性の顕著な減少が認められた。従って、 $x / n y$  値の望ましい範囲は 1.6 以上、2.4 以下である。これを  $y$  について整理すると、 $y$  値の望ましい範囲は下記の式で示される。

$$(x / (2.4 n)) \leq y \leq (x / (1.6 n))$$

【 0 0 1 2 】

(実施例 4)

A 元素として S r、R 元素として L a、M 元素として Z n をそれぞれ選択し、 $S r C O_3$ 、 $F e_2 O_3$ 、 $L a_2 O_3$  および  $Z n O$  を下記に示す化学式において、 $n = 5.85$ 、 $x = 2 n y$ 、 $x = 0.117$  になるよう配合し、湿式にて混合した後、 $1200^{\circ}C$  で



2 時間、大気中で仮焼した。仮焼粉をローラーミルで乾式粉碎を行い粗粉碎粉とした。その後、アトライターにより湿式粉碎を行い、平均粒径値が  $0.7 \mu m$  の微粉碎粉を含むスラリーを得た。磁石特性におよぼす焼結助剤の効果を調査するため、 $S i O_2$  と  $C a C O_3$  を粉碎粉に対する重量比でそれぞれ 0 ~ 0.60 %、0.80 % ( $C a O$  換算で 0.45 %) 粉碎初期に添加した。このスラリーを 10 k O e の磁場中で湿式成形を行い、成形体とした。この成形体を  $1180 \sim 1230^{\circ}C$  の温度範囲で 2 時間焼結し、焼結体とした。この焼結体を約  $10 \times 10 \times 20 mm$  の形状に加工し、B-H トレーサーにより磁石特性を評価した。結果を図 2 に示す。なお  $S i O_2$  が 0 % の場合は  $i H c$  値が極端に低くプロットしていない。

図 2 から  $S i O_2$  添加量の増加に伴い保磁力  $i H c$  値が増加し、0.45 % 添加時に適正な  $i H c$  が得られることがわかる。一方  $S i O_2$  添加量を更に増加し、0.60 % とした場合には、 $i H c$  の焼結温度に対する依存性が不安定となる。これは  $S i O_2$  の粒成長抑制効果が過剰となり、焼結時に適正な粒成長が進まなかったためと考えられる。従って、 $S i O_2$  添加量は重量百分比率で 0.40 % 以

上、0.50%以下が望ましいことがわかる。

以上は  $n = 5.85$  の場合の結果であるが、望ましい  $\text{SiO}_2$  添加量範囲には  $n$  値依存性がある。そこで  $n = 5.95$  で同様な検討を行った結果、この場合は重量百分比率で0.20%以上、0.50%以下の  $\text{SiO}_2$  添加量が望ましいことがわかった。

$\text{SiO}_2$  添加量を重量百分比率で0.45%と固定して、磁石特性の  $\text{CaO}$  添加量依存性を検討した結果、上記とほぼ同様な結果が得られ、これより  $\text{CaO}$  の望ましい添加量範囲は重量百分比率で0.35~0.55%であることがわかった。

次に、M元素として  $\text{Zn}$  に代えて  $\text{Co}$  を選択した以外は上記実施例4のものと同様にして作製した焼結体の磁石特性に及ぼす  $\text{SiO}_2$  と  $\text{CaO}$  の複合添加量の影響を調査した結果、重量百分比率で  $\text{SiO}_2$  添加量は0.20%以上、0.50%以下であるとともに  $\text{CaO}$  添加量は0.35~0.55%が望ましいことがわかった。

#### 【0013】

##### (実施例5)

R元素として  $\text{La}$ 、M元素として  $\text{Mn}$ 、 $\text{Co}$ 、 $\text{Ni}$ 、 $\text{Zn}$  をそれぞれ選択し、 $\text{SrCO}_3$ 、 $\text{Fe}_2\text{O}_3$ 、 $\text{La}_2\text{O}_3$  およびM元素の酸化物を下記に示す化学式において、 $n = 5.85$ 、 $x = 2ny$ 、 $x = 0.117$  になるよう配合し、湿式にて混合した後、1200℃で2時間、大気中で仮焼した。仮焼粉をローラーミルで乾式粉碎

$(\text{Sr}_{1-x}\text{La}_x)\text{O} \cdot n((\text{Fe}_{1-y}\text{M}_y)_2\text{O}_3)$  を行い粗粉碎粉とした。その後、アトライターにより湿式粉碎を行い、平均粒径が  $0.7\ \mu\text{m}$  の微粉碎粉を含むスラリーを得た。焼結助剤として、 $\text{SiO}_2$  と  $\text{CaCO}_3$  を粉碎粉に対する重量比でそれぞれ0.45%、0.80%( $\text{CaO}$ 換算で0.45%)粉碎初期に添加した。このスラリーを10kOeの磁場中で湿式成形を行い、成形体とした。この成形体を1180~1230℃の温度範囲で2時間焼結し、焼成体とした。また同様な方法で  $x = y = 0$  なる組成を有する試料を比較材(従来材)として作製した。この焼結体を約  $10 \times 10 \times 20\ \text{mm}$  の形状に加工し、B-Hトレーサーにより磁石特性を評価した。結果を図3に示す。

【図 2】

